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			5c. PROGRAM ELEMENT NUMBER 611103		
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14. ABSTRACT Simultaneous electronic and optical measurements provide a means of accessing microscopic information about the electronic and vibrational energy distributions in atomic- and molecular-scale systems driven out of equilibrium. These distributions and their evolution as a function of temperature, bias, and optical intensity are directly relevant to understanding the flow of energy and the origins of dissipation at the nanoscale, a topic of direct interest to the DoD. In support of a full research proposal awarded (by ARO, proposal 63808CH) in September, 2013, we sought critical integrated upgrades to our Raman microscopy system. The first was acquisition of a closed cycle					
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Report Title

Final Report: A Closed-Cycle Optical Cryostat and Improved Optical Elements for Studies of Dissipation at the Molecular Scale

ABSTRACT

Simultaneous electronic and optical measurements provide a means of accessing microscopic information about the electronic and vibrational energy distributions in atomic- and molecular-scale systems driven out of equilibrium. These distributions and their evolution as a function of temperature, bias, and optical intensity are directly relevant to understanding the flow of energy and the origins of dissipation at the nanoscale, a topic of direct interest to the DoD. In support of a full research proposal awarded (by ARO, proposal 63808CH) in September, 2013, we sought critical integrated upgrades to our Raman microscopy system. The first was acquisition of a closed-cycle cryocooled microscope cryostat system from Montana Instruments. The CryoStation allows optical and electronic measurements in high vacuum at sample temperatures down to 3 K, with no helium cost and vibrations limited to the few-nm scale. The instrument was integrated with our existing custom-built Raman microscope and software, previously demonstrated to allow single-molecule sensitivity Raman spectroscopy. The second component of our upgrade was a revamped ultranarrow optical notch filter and ultrastable laser source for measurements down to extremely low wavenumber Raman shifts. These upgrades have been incredibly valuable, and the new capabilities have transformed the way we are able to perform simultaneous electronic and optical measurements at the molecular scale.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
02/03/2016	1.00 Kenneth M. Evans, Pavlo Zolotavin, Douglas Natelson. Plasmon-Assisted Photoresponse in Ge-Coated Bowtie Nanojunctions, ACS Photonics, (08 2015): 0. doi: 10.1021/acsphotonics.5b00250
02/03/2016	2.00 Pavlo Zolotavin, Yajing Li, Peter Doak, Leeor Kronik, Jeffrey B. Neaton, Douglas Natelson. Interplay of Bias-Driven Charging and the Vibrational Stark Effect in Molecular Junctions, Nano Letters, (02 2016): 0. doi: 10.1021/acs.nanolett.5b04340
TOTAL:	2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

02/05/2016 3.00 Pavlo Zolotavin, Douglas Natelson. Plasmonic Heating in Au nanowires at Low Temperatures, ACS Nano (02 2016)

TOTAL: 1

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Charlotte I. Evans	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Pavlo Zolotavin	0.00
FTE Equivalent:	0.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Douglas Natelson	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

Final report: A closed-cycle optical cryostat and improved optical elements for studies of dissipation at the molecular scale

I. Statement of the problem

Simultaneous electronic and optical measurements provide a means of accessing microscopic information about the electronic and vibrational energy distributions in atomic- and molecular-scale systems driven out of equilibrium. These distributions and their evolution as a function of temperature, bias, and optical intensity are directly relevant to understanding the flow of energy and the origins of dissipation at the nanoscale, a topic of direct interest to the DoD. Achieving these measurement goals requires (1) a stable, extremely clean sample environment with access to temperatures down to a few Kelvin, to maximize energy resolution; (2) lack of appreciable vibrations or other positional instabilities, such that long data acquisition procedures may be employed to enhance signal-to-noise via averaging; and (3) high energy resolution, particularly down to the low energy limit associated with center of mass motion of molecules (a few meV = tens of cm^{-1}) and low-lying phonons of bulk solids (e.g., the Au optical phonon at 17 meV). To address these experimental needs, this project supported the acquisition of a closed-cycle optical cryostat from Montana Instruments, as well as a new 785 nm diode laser and ultrahigh resolution Bragg grating filters to examine inelastic light scattering down to a few cm^{-1} in energy.

II. Summary of the most important results

The addition of the cryogen-free, low-vibration optical cryostat from Montana Instruments (**Fig. 1**) was a significant improvement to our low temperature scanning Raman microscopy setup. Until the upgrade we used a conventional cold-finger cryostat from Cryo Industries specially designed for microscopy applications. The lowest sample temperature that we were able to achieve with the flow cryostat was 15K, which is a major drawback for the planned experiments on inelastic electron tunneling spectroscopy that require $T < 5\text{K}$ for optimal resolution. Additionally, the spatial position of the sample was (unintentionally) dependent on the cryogen flow rate because of the thermal expansion of the

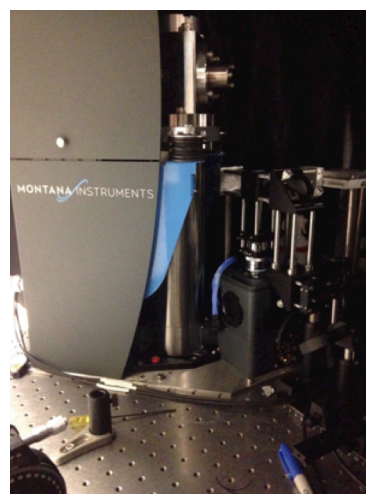


Fig. 1. Montana Instruments cryostation, as integrated into the Raman measurement

cryostat's internal components. Despite the long periods of equilibration after reaching base temperature, the sample would still drift as the cryogen flow rate was changing over time. *All of these problems were eliminated with installation of the new cryostat.* The lowest sample temperature we can reach is 4K. The sample temperature is maintained as long as needed, without necessity of periodic warm ups. The stabilization time is reduced from several hours to 20-30 minutes. The sample drift is completely eliminated. The new system also offers multiple logistical improvements for running experiments and overall time management. The ability to maintain samples continuously, for long periods, in a cryopumped vacuum environment has greatly enhanced sample cleanliness and longevity. Operation of the cryostat is completely automated and remotely controlled, liberating time for other activities. In many respects this was an enabling upgrade for this kind of experiments.

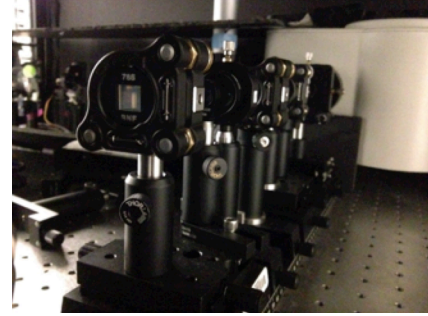


Fig. 2. OptiGrate Bragg notch filters integrated into the Raman measurement system.

Installation of ultra narrow notch filters (**Fig. 2**) based on the volumetric Bragg gratings manufactured by OptiGrate extended the capabilities of the set-up into the low-wavenumber region. The best conventional notch filters block an approximately 300 cm^{-1} region in the Raman spectrum near the laser line.

A conventional solution for this problem is either usage of a double spectrometer, which reduces signal intensity, or adjustment of the notch spectral position to acquire either Stokes or the anti-Stokes side of the Raman spectra. The new filter set allows for simultaneous acquisition on both sides of the laser line, as

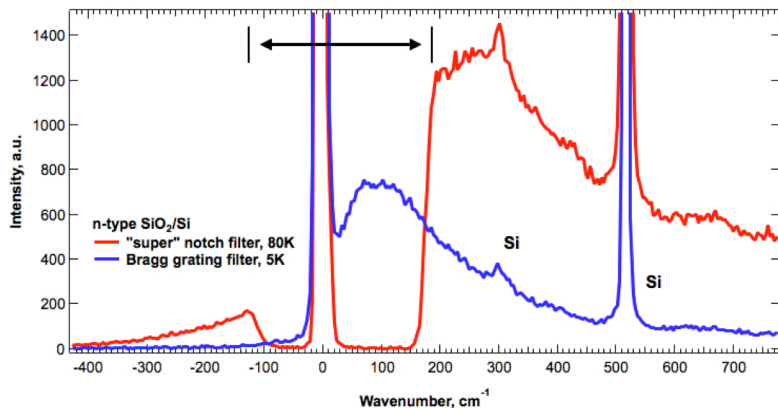


Fig. 3. Comparison of the Raman spectra of the test n-type SiO_2/Si wafer acquired at $T = 80\text{ K}$ using an old “super” notch filter (red) and using the new Bragg grating filter at 5K. Acquisition time for both spectra is 10 sec. Arrow demonstrates the spectral area blocked by the conventional notch filter.

demonstrated in **Fig. 3**. A downside to this filter system is that it requires a specially filtered narrow-line laser with small beam divergence. The spectrum shown in the figure is acquired with the old laser from ONDAX that was not performing to the specifications. This results in additional artifact lines around $\sim 80\text{-}100\text{ cm}^{-1}$. Initially we purchased a new laser from Innovative Photonics that was compatible with a Bragg filter set; however the laser was damaged during the shipment and after several rounds of negotiations we were refunded. We have acquired a new version of the current laser from ONDAX and are planning to install it imminently.

Figure 4 shows one example of the kind of investigation made possible by the new stability of the Montana

Instruments system.

From a paper in submission[1], the

figure shows the effect of plasmon-induced

optical heating on the temperature of a

plasmonically active nanowire on a SiO_2/Si

substrate. The local temperature rise due to

the incident light is inferred from the temperature-dependent resistivity of the Au film constituting the wire. The heating is considerably enhanced when the incident polarization is aligned transverse to the wire, coupling to the transverse plasmon mode (resonant with the incident 785 nm wavelength radiation). As substrate temperature is reduced down to 5 K (a condition only realizable with the new equipment supported by this award), optically induced heating is much more severe. The temperature rise exhibits a nontrivial dependence on the incident intensity due to the complicated, temperature-dependent thermal boundary resistance between the metal film and the underlying dielectric.

To summarize, these acquisitions have made possible experiments that simply would not have been achievable with the previous setup, including a transformative change toward long-baseline measurements and sample lifetime. Two papers[2, 3] have been published so far that

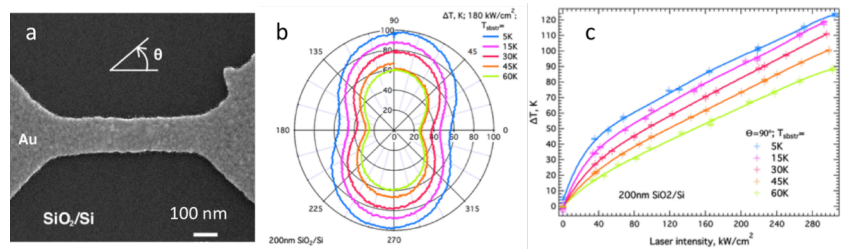


Fig. 4. Temperature increase for bowties fabricated on the SiO_2/Si substrate: (a) Scanning electron microscope (SEM) image of a typical device. Width of the device is $138 \pm 5\text{ nm}$, length is $600 \pm 30\text{ nm}$. (b) Polarization dependence of the light-driven temperature increase at different substrate temperatures for 180 kW/cm^2 laser intensity. (c) Dependence of the temperature increase on laser intensity; the laser focal spot diameter is $1.8\text{ }\mu\text{m}$. Lines through data points serve as a guide to the eye.

have taken advantage of these changes, with one[1] just submitted, and two more in process after that. These are just the beginning of a new era of operations made possible by the temperature range, stability, clean sample environment, and spectral regions now accessible thanks to the DURIP award.

Bibliography

1. Pavlo Zolotavin and Douglas Natelson, “Plasmonic Heating in Au nanowires at Low Temperatures”, *ACS Nano* (submitted, 2016).
2. Kenneth M. Evans, Pavlo Zolotavin, and Douglas Natelson, “[Plasmon-assisted photoresponse in Ge-coated bowtie junctions](#)”, *ACS Photonics* **2**, 1192-1198 (2015).
3. Yajing Li, Pavlo Zolotavin, Peter Doak, Leeor Kronik, Jeffrey B. Neaton, and Douglas Natelson, “[Interplay of Bias-Driven Charging and the Vibrational Stark Effect in Molecular Junctions](#)”, *Nano Lett.* (in press, 2016).